

EFFECT OF CURING CONDITIONS ON THE POROSITY CHARACTERISTICS OF METAKAOLIN-FLY ASH GEOPOLYMERS

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ABSTRACT

The porosity characteristics of metakaolin (MK)- and fly ash (FA)-based geopolymers cured under ambient, thermal, and moist conditions were investigated using nitrogen adsorption porosimetry. In general, surface areas were higher for materials prepared from FA (29.0–59.2 m²/g) than for MK (5.3–12.8 m²/g). Total pore volumes ranged from 0.034–0.104 cc/g for MK-based materials and from 0.077–0.089 cc/g for FA-based materials. For MK-based geopolymers, curing under ambient conditions resulted in a single, broad pore size distribution (PSD) between 250–500 Å. PSDs for MK-based geopolymers cured using thermal or moist methods were bimodal with broad peaks between approximately 60–250 Å and 250–500 Å. For FA-based geopolymers, a single, broad PSD was observed and ranged from 20–100 Å for ambient temperature cured materials and 40–200 Å for materials cured under thermal or moist conditions. The observed pore size distributions were accompanied by a shift to higher wavenumber in the position of the main geopolymer band in the ATR-FTIR spectra of geopolymer materials after thermal or moist curing, indicating a higher concentration of Si–O–Si bonds formed in the materials cured at elevated temperatures. These results suggest that the observed PSDs result from Si–O–Al and Si–O–Si bond formation during curing and are affected by the curing conditions.

INTRODUCTION

Curing conditions have been shown to affect mechanical strength development and cracking tendency in geopolymers prepared from metakaolin or fly ash. For example, Palomo *et al.* investigated the effect of curing at elevated temperatures (65–95°C) on the mechanical strength of FA geopolymers¹. Bakharev showed the beneficial effect of pre-curing at room temperature on the strength properties of FA-derived geopolymers². Kovalchuk *et al.* showed that temperature and humidity play key roles in the development of the microstructure and properties of alkali-activated FA materials³. Perera *et al.* investigated the influence of curing schedule on the porosity and cracking tendency of metakaolinite-based geopolymers and found that curing at higher relative humidity does not offer an advantage over curing at ambient followed by heating (40–60°C) in sealed containers⁴. From these studies, it is clear that the effects of curing conditions depend on various factors including source material, temperature, humidity, and curing time and must be considered for each individual geopolymer system.

To complement previous studies, this paper presents a systematic investigation of the effects of curing conditions on the porosity characteristics of geopolymers prepared from MK or FA as determined using nitrogen adsorption porosimetry.

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EXPERIMENTAL

Materials

The aluminosilicate source materials were MK (Powerpozz, Advanced Cement Technologies) and class F FA (Boral Material Technologies). MK contained 54–56 % SiO_2 and 40–42 % Al_2O_3 . FA contained 53.94 % SiO_2 , 28.25 % Al_2O_3 , and 7.29 % Fe_2O_3 . Sodium silicate D (PQ Corporation) and potassium hydroxide pellets (Aldrich or Fisher) were used. Sodium silicate D contains 29.4 % SiO_2 and 14.7 % Na_2O .

Particle size distributions of the aluminosilicate source materials were determined using an APS 3321 particle size analyzer (TSI Inc.). The mean particle sizes of MK and FA were 0.89 and 1.1 μm , respectively. The specific gravities reported by the manufacturer for MK and FA were 2.60 and 2.28 g/cm^3 , respectively. The Brunauer–Emmet–Teller (BET) surface areas (0.05–0.3 P/Po) of MK (16.5 m^2/g) and FA (2.3 m^2/g) were measured using an Autosorb-1 porosimeter (Quantachrome Inc.) using N_2 adsorbate at 77 K.

Geopolymer Formulation and Synthesis

Geopolymer compositions were prepared using $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$ and $\text{M}_2\text{O}/\text{SiO}_2 = 1.75$. The $\text{H}_2\text{O}/\text{M}_2\text{O}$ ratio was 11 and 2 for materials prepared using metakaolin and fly ash, respectively. In a typical preparation, sodium silicate and potassium hydroxide were mixed and allowed to cool to room temperature. The solid components were then added with vigorous mixing using a rotary mixer for 10 minutes. The materials were transferred into plastic molds, covered with a plastic top, and allowed to cure at room temperature overnight. Room temperature cured specimens were then allowed to cure, covered, for 28 days. Thermally cured specimens were covered and placed in a 90°C oven for 5 days. Moist cured specimens were placed, uncovered, in an environmental chamber at 52°C and 85% relative humidity for 14 days.

Nitrogen Adsorption

N_2 adsorption/desorption analysis at 77K was performed on powdered specimens using an Autosorb 1 porosimeter (Quantachrome Inc.). Prior to analysis, air/water desorption was typically carried out at 200°C overnight. Surface area was calculated using the BET method in the $0.05 \leq P/P_0 \leq 0.3$ region. Total pore volume was determined at $P/P_0 = 0.995$. Pore size distributions were determined using the adsorption data and the non-local density functional theory (NLDFT) method provided in the ASWin 2.0 porosimeter software. The NLDFT kernel used for data analysis was for N_2 adsorbate on a zeolite adsorbent at 77K.

RESULTS AND DISCUSSION

Nitrogen adsorption/desorption was used to investigate the surface area, total pore volume, and pore size distribution of the MK- or FA-based geopolymer materials as a function of curing method. Figure 1 shows the N_2 adsorption/desorption isotherms of the geopolymers cured under room temperature, thermal, or moist curing conditions. The isotherms were Type IV⁵ and revealed capillary condensation accompanied by a hysteresis loop of varying widths, indicating the presence of mesoporosity.

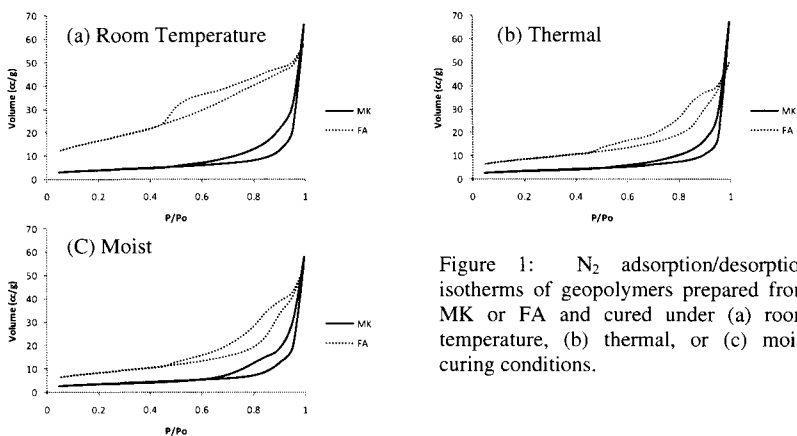


Figure 1: N_2 adsorption/desorption isotherms of geopolymers prepared from MK or FA and cured under (a) room temperature, (b) thermal, or (c) moist curing conditions.

BET surface areas were calculated using the linear portion of the isotherm between 0.05–0.3 P/P_0 . Figure 2 shows the BET surface area of the MK- and FA-based materials cured under room temperature, thermal, or moist conditions. The BET surface areas were 5.3, 11.9, and 12.8 m^2/g for the MK-based geopolymers cured, respectively, under RT, thermal, or moist conditions. The respective BET surface areas for the FA-based geopolymers cured under room temperature, thermal, or moist conditions were 59.2, 29.8, and 29.0 m^2/g . The significantly higher surface area for the FA-based materials cured under ambient conditions may indicate a lower extent of polycondensation as compared to MK-based materials. For either MK or FA, the BET surface areas for the thermal- and moist-cured materials were similar.

Total pore volume (TPV) is derived from the amount of nitrogen vapor adsorbed at a relative pressure close to unity by assuming that the pores are then filled with condensed adsorbate in the normal liquid state. Due to the lack of a plateau at high P/P_0 , TPVs in this study were calculated at $P/P_0=0.995$. Figure 3 shows the effect of curing condition on the TPV of the MK- and FA-based materials. For room temperature curing, the TPV of the FA-based geopolymer was significantly higher than that of the analogous MK-based material, presumably due to the

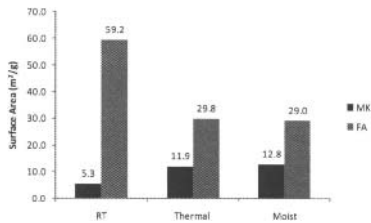


Figure 2: Surface area of MK- or FA-based geopolymers as a function of curing method.

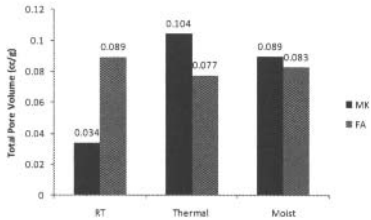


Figure 3: Total pore volume of MK- or FA-based geopolymers as a function of curing method.

more porous, less-condensed nature of these materials. The TPV of materials prepared using thermal or moist curing methods was similar, ranging from 0.077–0.104 cc/g. The TPV for the MK-based geopolymers cured under thermal or moist conditions were higher than for the analogous material cured under ambient conditions, possibly due to a broader distribution of pores.

Non-local density functionally theory is commonly used for the determination of PSD for micro- and mesoporous materials⁶. Figure 4 shows the NLDFT PSDs of the MK- and FA-based materials cured using room-temperature, thermal, or moist curing methods. For the MK-based materials cured under ambient conditions, the PSD was observed in the 250–500 Å region. The PSDs for MK-based materials cured under thermal or moist conditions were bimodal, with broad peaks between approximately 60–250 Å and 250–500 Å. The PSD for FA-based materials cured at room temperature was observed at approximately 20–100 Å. For the FA-based materials, the PSD was observed predominately between 40–200 Å for materials cured using thermal or moist conditions. The observed pore size distributions were accompanied by a shift to higher wavenumber in the position of the main geopolymer band in the ATR-FTIR spectra (not shown) during thermal or moist curing, indicating a higher concentration of Si–O–Si bonds are formed in the materials cured at elevated temperatures.

Geopolymer materials comprise the aluminosilicate gel, unreacted or partially reacted aluminosilicate source materials (amorphous or crystalline), and porosity. The porosity that develops is expected to result from (a) condensation of released $\text{Al}(\text{OH})_4^-$ ions with the silicate to form Si–O–Al bonds and (b) silicate–silicate condensation to form Si–O–Si bonds. The three curing methods under investigation involve different combinations of water and thermal contact, influencing the relative rates of dissolution, hydrolysis, and condensation. For MK-based geopolymers cured under ambient conditions, the single PSD between 250–500 Å suggests this peak is due primarily to Si–O–Al bond formation due to silicate– $\text{Al}(\text{OH})_4^-$ condensation. The shift in the ATR-FTIR band position of geopolymers cured under thermal or moist conditions indicates that the growth of the broad 60–250 Å peak in the PSD of the MK-based geopolymers is likely due to the formation of Si–O–Si bonds due to thermally-induced silicate–silicate condensation. The single, broad peak in the pore size distribution of FA-based materials cured under thermal or moist conditions may be related to predominately Si–O–Si bond formation through thermally-induced silicate–silicate condensation occurring in the absence of a high rate of release of $\text{Al}(\text{OH})_4^-$ ions from FA. To confirm this, additional studies related to the microstructure and connectivity of MK- and FA-based geopolymers as a function of curing conditions will be conducted.

CONCLUSIONS

Porosity characteristics (surface area, total pore volume) and pore size distributions of geopolymeric materials were affected by curing conditions. N_2 adsorption porosimetry showed that MK- or FA-based geopolymers were mesoporous. A shift to higher wavenumber in the position of the main geopolymer band in the ATR-FTIR spectra of geopolymer materials after thermal or moist curing indicated a higher concentration of Si–O–Si bonds formed in the materials cured at elevated

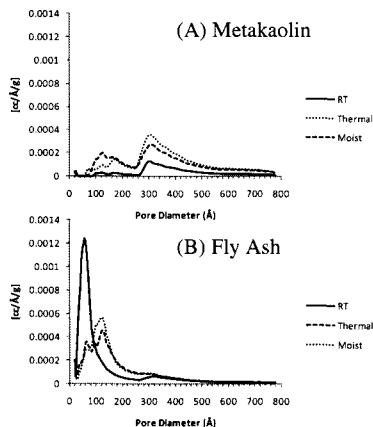


Figure 4: NLDFT pore size distributions for (a) MK- and (b) FA-based geopolymers cured under room temperature, thermal, or moist conditions.

temperatures. MK-based geopolymers cured under thermal or moist conditions exhibited bimodal pore size distributions due to silicate oligomer- $\text{Al}(\text{OH})_4^-$ condensation (Si-O-Al bond formation) and thermally-induced silicate-silicate condensation (Si-O-Si bond formation). FA-based geopolymers cured under thermal or moist conditions exhibited a single, broad pore size distribution due primarily to Si-O-Si bond formation caused by thermally-induced silicate-silicate condensation and the lower $\text{Al}(\text{OH})_4^-$ release rates for FA as compared to MK.

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